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SYNTHESIS AND CHARACTERIZATION OF $(Me_3SiCH_2)_3M{\bullet}E(SiMe_3)_3$, (M = Ga, E = P or As; M = In, E = P). X-RAY CRYSTAL STRUCTURES OF $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ AND $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$.

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The reaction of $(Me_3SiCH_2)_3Ga$ with $P(SiMe_3)_3$ or $As(SiMe_3)_3$ in a 1:1 mole ratio affords the simple adducts $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3Ga{\bullet}As(SiMe_3)_3$ (**2**), respectively. Combining $(Me_3SiCH_2)_3In$ with $P(SiMe_3)_3$ in a 1:1 mole ratio yields the adduct $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$ (**3**), in a nearly quantitative yield.

The solid-state structures of **1** and **3** were established by X-ray crystallography. Isomorphous **1** and **3** crystallize in the trigonal system, space group $P3_1$, with a = 16.027(3), c = 11.9928(18) Å, V = 2667.9(7) Å^3, Z = 3, $D_{calc.}$ = 1.087 g cm^{-3} for **1**, and a = 16.061(8), c = 12.0913(19) Å, V = 2701.0(13) Å^3, Z = 3, $D_{calc.}$ = 1.156 g cm^{-3} for **3**. Full-matrix least-quares refinement based on 3397 (**1**) and 4156 (**3**) reflections with $I > 2.5\sigma$ converged at R = 0.059 (R_w = 0.062) and R = 0.039 (R_w = 0.044), respectively. Metal-pnicogen bond lengths were found to be: Ga-P = 2.646 Å, and In-P = 2.771 Å. The thermal decomposition behavior of **1** - **3** was examined by TGA-DTA. These studies indicated that compounds **1** and **2** eliminated their organic ligands in a stepwise manner, while compound **3** decomposed in a single-step process.

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Summary—The reaction of $(Me_3SiCH_2)_3Ga$ with $P(SiMe_3)_3$ or $As(SiMe_3)_3$ in a 1:1 mole ratio affords the simple adducts $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3Ga{\bullet}As(SiMe_3)_3$ (**2**), respectively. Combining $(Me_3SiCH_2)_3In$ with $P(SiMe_3)_3$ in a 1:1 mole ratio yields the adduct $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$ (**3**), in a nearly quantitative yield.

The solid-state structures of **1** and **3** were established by X-ray crystallography. Isomorphous **1** and **3** crystallize in the trigonal system, space group $P3_1$, with a = 16.027(3), c = 11.9928(18) Å, V = 2667.9(7) Å^3, Z = 3, $D_{calc.}$ = 1.087 g cm^{-3} for **1**, and a = 16.061(8), c = 12.0913(19) Å, V = 2701.0(13) Å^3, Z = 3, $D_{calc.}$ = 1.156 g cm^{-3} for **3**. Full-matrix least-

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squares refinement based on 3397 (**1**) and 4156 (**3**) reflections with $I > 2.5\sigma$ converged at $R = 0.059$ ($R_w = 0.062$) and $R = 0.039$ ($R_w = 0.044$), respectively. Metal-pnicogen bond lengths were found to be: Ga-P = 2.646 Å, and In-P = 2.771 Å. The thermal decomposition behavior of **1 - 3** was examined by TGA-DTA. These studies indicated that compounds **1** and **2** eliminated their organic ligands in a stepwise manner, while compound **3** decomposed in a single-step process.

INTRODUCTION

Recent investigations in our laboratory have centered on the facile formation of the 13-15 bond by reactions of organo-group 13 reagents with either the silylpnicogen compounds $E(SiMe_3)_3$ (E = P or As) or their monolithium salts in solution[1]. As a result of our efforts, we have isolated several new compounds containing the 13-15 covalent bond. Included in our results are compounds which exhibit dimeric structures in the solid-state[2] and those in which two group 13 centers are bridged by a halogen atom and a group 15 atom[2]. In addition, adducts of the type $R_3M{\bullet}E(SiMe_3)_3$ (R = Me_3SiCH_2, M = In, E = As[3]; R = Ph[3] or C_6F_5[4], M = Ga, E = As or P) have been isolated in our laboratory. Adducts of this type may find utility as potential single-source precursors to binary 13-15 semiconductors[5]; however, a review of the literature finds limited structural and thermal analysis data for adducts of this type. We report herein the synthesis, characterization, and thermal analysis of three new main group adducts, $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (**1**), $(Me_3SiCH_2)_3Ga{\bullet}As(SiMe_3)_3$ (**2**), and $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$ (**3**).

EXPERIMENTAL

General Considerations

All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Pentane was distilled over $LiAlH_4$ under dry dinitrogen. Literature procedures were used to prepare and purify $P(SiMe_3)_3$[6], $As(SiMe_3)_3$[7], $(Me_3SiCH_2)_3Ga$[8] and $(Me_3SiCH_2)_3In$[9]. The

integrity of all materials used was confirmed via ^1H NMR spectra. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 121.4 MHz, respectively and a Varian Unity 500 spectrometer operating at 500, 125.7, and 202.3 MHz, respectively. ^1H and $^{13}C\{^1H\}$ spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. $^{31}P\{^1H\}$ spectra were referenced externally to H_3PO_4 at δ 0.00 ppm. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. All melting points (uncorrected) were obtained on a Thomas-Hoover Uni-melt apparatus and the melting point capillaries were flame-sealed under argon. Thermo-Gravimetric Analysis/Differential Thermal Analysis data were collected on a TA Instruments SDT 2960 simultaneous TGA-DTA instrument. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. X-ray crystallographic analyses were conducted in the Single Crystal X-ray Structure Center at the University of North Carolina at Chapel Hill.

Preparation of $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (1)

Inside the dry-box, a one-necked 250 mL round-bottomed flask equipped with a Teflon valve was charged with pentane (30 mL) and $(Me_3SiCH_2)_3Ga$ (0.331 g, 0.999 mmol) furnishing a clear solution to which was added dropwise $P(SiMe_3)_3$ (0.250 g, 0.998 mmol) in pentane (30 mL). The resulting clear solution was stirred outside of the dry-box for 48 h at room temperature. Following removal of the volatiles *in vacuo*, the crude crystalline product was dissolved in warm pentane (5 mL). Upon cooling to -15 °C for several days, colorless, air-sensitive crystals of **1** formed; 0.564 g, 97% yield, mp. 48 - 53 °C. Anal. Calcd. for $C_{21}H_{60}GaPSi_6$: C, 43.34 H, 10.39. Found: C, 43.02 H, 10.23. ^1H NMR: δ 0.272 [d, $SiMe_3$ (J_{P-H} =4.5 Hz)], 0.078 (s, CH_2), 0.109 (s, C-$SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 4.066 [d, $SiMe_3$ (J_{P-C} = 10.9 Hz)], 2.543 (s, CH_2), 12.247 (s, Me_3). $^{31}P\{^1H\}$ NMR: δ -248.98 (s).

Preparation of $(Me_3SiCH_2)_3Ga•As(SiMe_3)_3$ (2)

[Compound (**2**) was synthesized in the manner described for (**1**).]

Reactants: $(Me_3SiCH_2)_3Ga$ (0.331 g, 0.999 mmol), $As(SiMe_3)_3$ (0.294 g, 0.998 mmol).

Product: 0.501 g, 80% yield, mp. 43 - 50 °C. Anal. Calcd. for $C_{21}H_{60}GaAsSi_6$: C, 40.30 H, 9.66. Found: C, 39.91 H, 9.54. ^1H NMR: δ 0.343 (s, $SiMe_3$) , 0.120 (s, CH_2), 0.132 (s, C-$SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 4.066 (s, $SiMe_3$), 2.543 (s, CH_2), 12.247 (s, Me_3).

Preparation of $(Me_3SiCH_2)_3In•P(SiMe_3)_3$ (3)

[Compound (**3**) was synthesized in the manner described for (**1**).]

Reactants: $(Me_3SiCH_2)_3In$ (0.376 g, 0.999 mmol), $P(SiMe_3)_3$ (0.250 g, 0.998 mmol).

Product: 0.613 g, 98% yield, mp. 125 - 127 °C. Anal. Calcd. for $C_{21}H_{60}InPSi_6$: C, 40.23; H, 9.65. Found: C, 39.97; H, 9.43. ^1H NMR: δ 0.244 [d, $SiMe_3$ (J_{P-H} =5.0 Hz)], -0.112 (s, CH_2), 0.295 (s, C-$SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 3.538 [d, $SiMe_3$ (J_{P-C} = 9.1 Hz)], 3.239 (s, CH_2), 5.235 (s, Me_3). $^{31}P\{^1H\}$ NMR: δ -241.80 (s).

X-ray structural solution and refinement

Crystallographic data are summarized in Table 1. Colorless crystals of **1** and **3** were mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -135 °C on a Rigaku AFC6/S diffractometer utilizing graphite-monochromated Mo-Kα radiation (λ = 0.71073Å), and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counting-statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at R = 0.059 (R_w = 0.062) for **1**, and R = 0.039 (R_w = 0.044) for **3**. A final difference-Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX[10] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 11. Interatomic distances and angles

are given in Tables 2 - 4. ORTEP[12] diagrams showing the solid-state conformations and atom numbering schemes of **1** and **3** are presented in Figures 1 and 2. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, thermal and positional parameters, and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Centre.

RESULTS and DISCUSSION

The 1:1 mole ratio reaction of $(Me_3SiCH_2)_3Ga$ with $E(SiMe_3)_3$ (E = P or As) at room temperature affords the simple adducts **1** and **2** in high yields. Similarly, compound **3** results from the 1:1 mole reaction of $(Me_3SiCH_2)_3In$ and $P(SiMe_3)_3$ in pentane solution. Compounds **1** and **3** are white crystalline materials which are stable over long periods of time under inert atmosphere. Compound **2**, however, decomposes from a white crystalline solid to an orange liquid upon long standing. All three compounds are extremely sensitive to air and moisture and decompose rapidly upon exposure. The ^1H and ^{13}C NMR spectra of **1** - **3** confirm that these compounds do not dissociate in solution at room temperature and are pure prior to recrystallization.

The solid-state structures of **1** and **3** were determined by single-crystal X-ray analysis. The inability to isolate a suitable crystal of **2** precluded its structural determination. Compound **1** is one of a few crystallographically characterized 1:1 Ga-P adducts. Those whose structures have been determined are: $(Me_3CCH_2)_3Ga{\bullet}P(H)Ph_2$ (**4**)[13], $Ph_3Ga{\bullet}P(SiMe_3)_3$ (**5**)[14], $Ph_2(Cl)Ga{\bullet}P(SiMe_3)_3$ (**6**)[14], $Me_2(Cl)Ga{\bullet}PPh_2CH_2PPh_2$ (**7**)[15], $Cl_3Ga{\bullet}PMe_3$ (**8**)[16], and $I_3Ga{\bullet}PPh_3$ (**9**)[17]. In addition, the 2:1 complex $(Me_3Ga)_2{\bullet}(PPh_2CH_2)_2$ (**10**)[18] was also characterized in this manner. The Ga-P bond length of 2.646 Å in **1** is within the established range of lengths previously observed [the shortest being 2.353 (2) Å in **8** and the longest being 2.6853 (5) Å in **4**]. The elongated bond length in **1** is most likely due to the steric repulsions between the trimethylsilyl groups and the bulky trimethylsilylmethyl ligands. These repulsions

are also evidenced by the staggered conformation between the Me_3SiCH_2 and Me_3Si moieties. The coordination geometry about the gallium center is that of a distorted tetrahedron with a mean C-Ga-C angle of 116.7° and a mean C-Ga-P angle of 100.3°. Mean bond angles at the P atom [Ga-P-Si = 113.4° > Si-P-Si = 105.3°] reflect the relayed effect of the steric compressions resulting from the angular deformations around Ga.

Crystallographic information on simple organoindium-phosphorus adducts is scant and is limited to $(Me_3CCH_2)_3In{\bullet}P(SiMe_3)_3$ (**11**)[19], $Me(Me_3CCH_2)_2In{\bullet}P(SiMe_3)_3$ (**12**)[19], and $(Me_3In)_2{\bullet}(PPh_2CH_2)_2$ (**13**)[17]. The unit cell in **3** consists of discrete monomeric units with the In-P bond length being 2.771 Å. This is within range of the lengths previously observed in compounds **11** - **13** [the shortest being 2.755 (4) Å in **13** and the longest being 2.944 (4) Å in **11**]. The mean P-Si and In-C bond lengths at 2.276 Å and 2.210 Å, respectively in **3** are nearly identical to the average P-Si [2.271 Å] and In-C [2.213 Å] in **11**, whereas the angles around the In atoms [P-In-C = 101.43°, C-In-C = 116.18° for the mean values in **3**; P-In-C = 95.5°, C-In-C = 119.1° in **11**] differ significantly. These observed bond angle variations may be directly related to the fact that the C-C distances in Me_3CCH_2 groups are substantially shorter than Si-C bonds in Me_3SiCH_2 moieties thereby increasing the severity of the steric crowding in **11** vs **3**; although, the bond lengths should reflect this steric difference as well.

The potential for compounds **1** - **3** to serve as single-source precursors to 13-15 semiconductor materials motivated our study of their thermal decomposition behavior. Ideally, we desired that these adducts would completely eliminate their organic substituents at moderate thermal conditions (< 450 °C) with the resultant formation of the desired 13-15 material. Subsequently, we performed Thermo-Gravimetric Analysis studies on milligram quantities of **1** - **3**. Samples were heated at a rate of 5 °C/min. under a stream of nitrogen. The resulting TGA-DTA plots for each adduct **1** - **3** are given in the supplementary material. From these data, we concluded that compounds **1** and **2** undergo stepwise elimination of the organic ligands, while compound **3** decomposes in a single-step process. For each decomposition, it is important to note that weight percentages correponding to GaP, GaAs, and InP, respectively were observed

for the remaining decomposition residues, however, no further analysis was done to characterize these residues.

The results seen in the small-scale decompositions of **1** - **3** prompted us to attempt large-scale decompositions utilizing the thermal information gained from the TGA-DTA data. First, the adducts were placed in a vacuum sublimator and heated from 30 - 300 °C in ten degree increments under dynamic vacuum. Each of the adducts sublimed onto the sublimator cold-finger at temperatures less than 125 °C, and no decomposition was seen. Under argon atmosphere, adduct sublimation was somewhat hindered and the adducts changed phase from solid to liquid at 200 °C. The result at 300 °C was refluxing of the adducts on the sublimator cold finger and a small amount of oily residue at the bottom of the sublimator. No material which could be characterized as GaP, GaAs, or InP was obtained. These decomposition experiments were followed by attempts to decompose the adducts in a high-temperature tube furnace. Each of the adducts was sealed in a thick-walled glass tube and placed into the tube furnace under atmospheric pressure. The samples were heated to 400 °C for eight hours. In each case, the result was an oily residue which did not yield any viable product.

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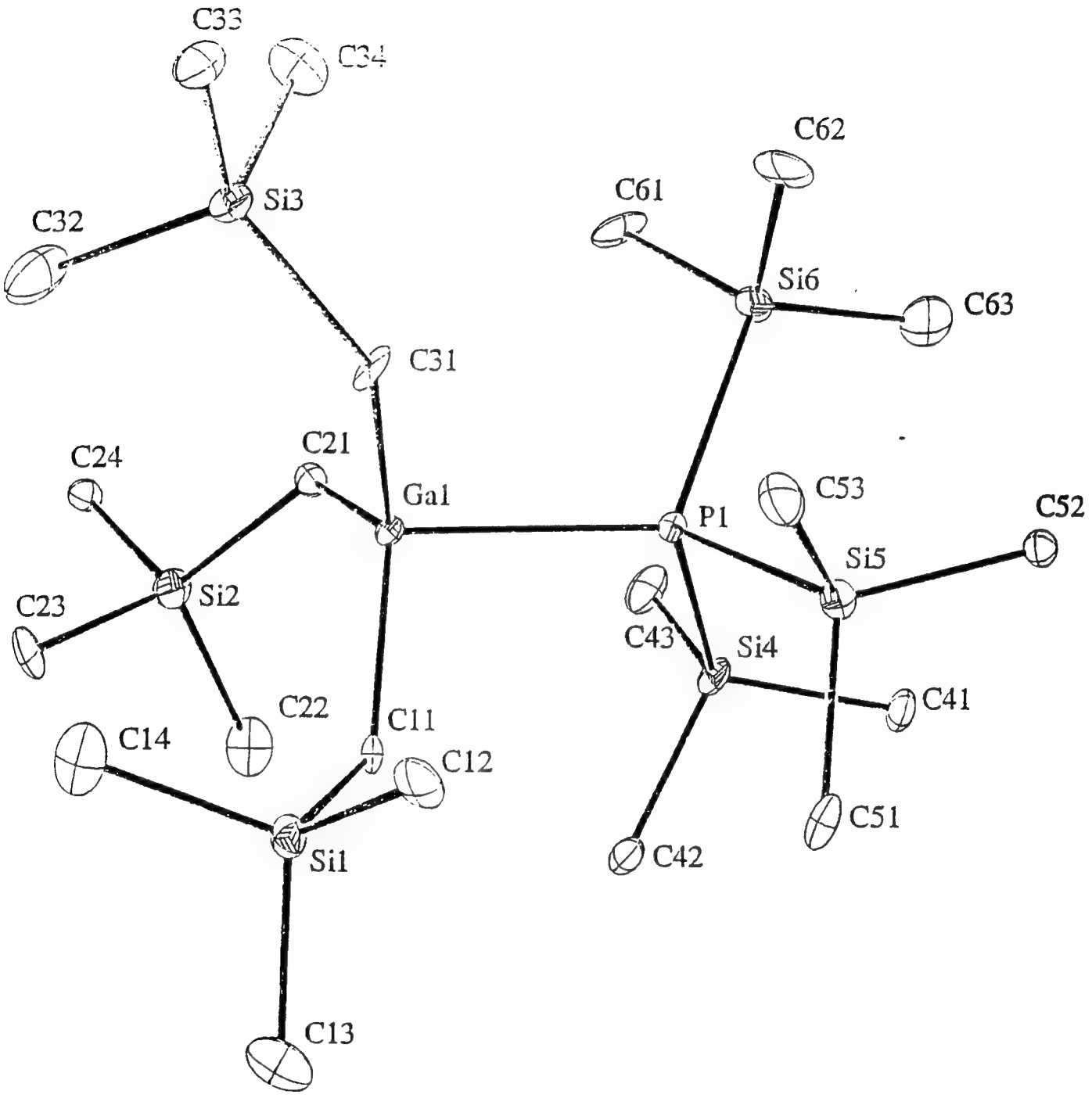
Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **1**. Hydrogen atoms are omitted for clarity.

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **3**. Hydrogen atoms are represented by small circles.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C32
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C21
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C53
C52
P1
Si5
C23
Si2
C43
Si4
C41
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C14
C12
C51
Si1
C42
C13
C62
C61
Si6
C63

Figure 1

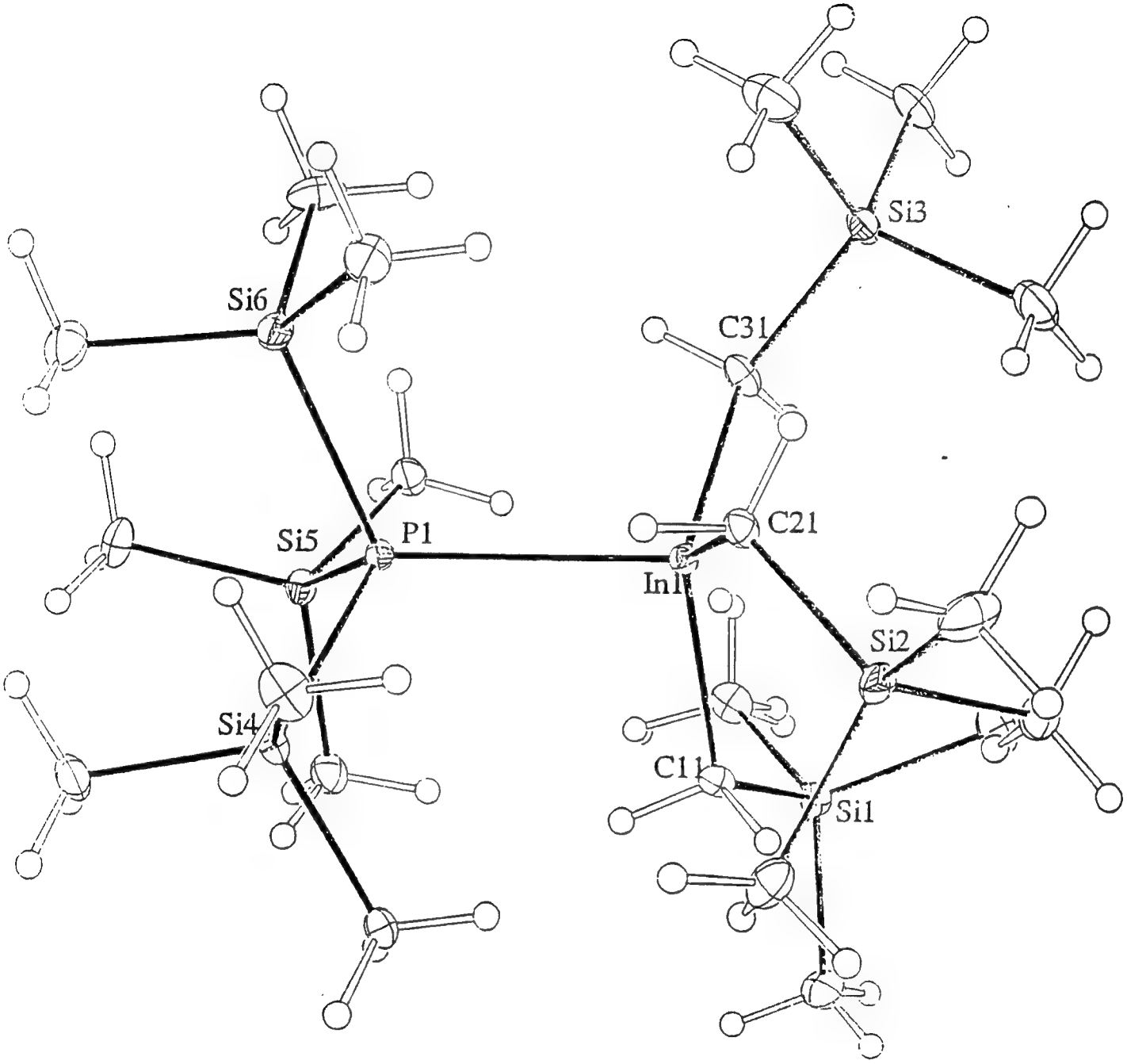

Figure 2

Table 1. Crystallographic Data and Measurements for $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (**1**), and $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$ (**3**)

	1	**3**
molecular formula	$C_{21}H_{60}Ga_1P_1Si_6$	$C_{21}H_{60}In_1P_1Si_6$
formula weight	581.91	627.01
crystal system	trigonal	trigonal
space group	$P3_1$	$P3_1$
a, Å	16.027(3)	16.061(8)
c, Å	11.9928(18)	12.0913(2)
V, A^3	2667.8(7)	2701.0(1)
Z	3	3
Radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, cm^{-1}	10.2	8.9
temp, C	-135	-135
D_{calcd}, g cm^{-3}	1.087	1.156
crystal dimens., mm	0.40 x 0.30 x 0.25	0.38 x 0.32 x0.25
T_{max}; T_{min}	0.782:0.626	0.804:0.727
scan type	ω	ω
scan width, deg	1.00	1.00
Θ_{max}, deg	50	60
No. of rflns rec.	5284	5466
No. of non-equiv. rflns recorded	5284	5224
No. of rflns retained, $I > 2.5\sigma(I)$	3397	4156
No. of parameters refined	261	262
R: R_w[a]	0.059; 0.062	0.039; 0.044
goodness-of-fit[b]	1.32	1.08
Max shift / esd. in final least-squares cycle	0.013	0.001

Table 1 (continued)

	1	3
Final max, min $\Delta\rho$, e/Å^{-3}	0.830; -0.780	0.890; -0.760

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w (|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$.

[b] Goodness-of-fit = $[\Sigma w \Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table 2. Selected bond distances (Å) and bond angles (°) for **1**. with Estimated Standard Deviations in Parentheses

Bond Lengths			
Ga1-P(1)	2.646(3)	Ga1-C(31)	2.019(15)
Ga1-C(11)	2.014(14)	P(1)-Si(5)	2.284(5)
Ga1-C(21)	2.025(14)		
Bond Angles			
P(1) - Ga(1) - C(11)	98.4(4)	C(11) - Ga(1) - C(31)	116.5(6)
Ga(1) - P(1) - Si(5)	113.54(19)	Si(4) - P(1) - Si(5)	106.25(21)
P(1) - Si(4) - C(42)	109.8(5)	C(11) - Si(1) - C(14)	112.9(7)
C(13) - Si(1) - C(14)	108.0(8)	Ga(1) - C(31) - Si(3)	119.7(8)

Table 3. Selected bond distances (Å) and bond angles (°) for **3**, with Estimated Standard Deviations in Parentheses

		Bond Lengths	
In1-P(1)	2.7713(15)	In1-C(31)	2.207(6)
In1-C(11)	2.206(6)	P(1)-Si(5)	2.2809(23)
In1-C(21)	2.218(6)		
		Bond Angles	
P(1) - In(1) - C(11)	98.45(16)	P(1) - Si(4) - C(42)	109.39(20)
C(11) - In(1) - C(31)	117.53(22)	C(11) - Si(1) - C(14)	111.1(3)
In(1) - P(1) - Si(5)	112.73(7)	C(13) - Si(1) - C(14)	108.6(3)
Si(4) - P(1) - Si(5)	107.56(8)	In(1) - C(31) - Si(3)	117.7(3)

Table 4. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for **1**. with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{iso}(Å^2)$[a]
Ga	-0.32356(11)	-0.33654(13)	-0.82776(-)	0.93(8)
P	-0.3380(3)	-0.3255(3)	-0.6091(3)	1.11(18)
Si(1)	-0.0930(3)	-0.2016(3)	-0.9218(4)	1.58(21)
Si(2)	-0.4372(3)	-0.2556(3)	-0.9888(4)	2.05(23)
Si(3)	-0.4041(3)	-0.5558(3)	-0.9407(4)	1.82(23)
Si(4)	-0.3518(3)	-0.1957(3)	-0.5596(4)	1.56(22)
Si(5)	-0.2086(3)	-0.3119(3)	-0.5133(4)	1.50(22)
Si(6)	-0.4678(3)	-0.4539(3)	-0.5306(4)	1.70(21)
C11	-0.1992(10)	-0.2119(10)	-0.8509(12)	1.4(8)
C12	-0.0401(10)	-0.2621(11)	-0.8364(14)	2.3(8)
C13	-0.0009(11)	-0.0717(13)	-0.9359(15)	3.0(9)
C14	-0.1205(12)	-0.2559(13)	-1.0637(14)	3.0(10)
C21	-0.4449(10)	-0.3378(10)	-0.8774(12)	1.4(7)
C22	-0.3938(11)	-0.1348(13)	-0.9304(14)	2.7(10)
C23	-0.3510(13)	-0.2428(12)	-1.1022(14)	3.6(11)
C24	-0.5578(10)	-0.2968(10)	-1.0546(13)	1.5(7)
C31	-0.3178(10)	-0.4589(10)	-0.8449(13)	1.8(8)
C32	-0.4099(14)	-0.5104(13)	-1.0815(17)	4.1(11)
C33	-0.3708(12)	-0.6522(11)	-0.9636(14)	2.7(9)
C34	-0.5307(12)	-0.6203(12)	-0.8830(15)	3.0(10)
C41	-0.3321(10)	-0.1678(11)	-0.4105(12)	2.0(8)
C42	-0.2620(11)	-0.0869(10)	-0.6387(13)	2.0(8)
C43	-0.4776(12)	-0.2216(12)	-0.5921(14)	2.8(9)
C51	-0.1050(11)	-0.1871(11)	-0.5340(13)	2.2(8)
C52	-0.2311(10)	-0.3360(10)	-0.3609(12)	1.4(7)
C53	-0.1787(12)	-0.3994(12)	-0.5727(14)	2.8(9)
C61	-0.5752(11)	-0.4870(11)	-0.6195(16)	2.8(9)
C62	-0.4466(11)	-0.5566(11)	-0.5258(15)	3.1(9)
C63	-0.4927(11)	-0.4288(13)	-0.3851(16)	3.7(10)

[a]B_{iso} = the mean of the principal axes of the thermal ellipsoid

Table 5. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for **3.** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{iso}(Å^2)^a$
In	0.32963(3)	0.31798(2)	0.20454(-)	0.985(2)
P	0.34260(1)	0.34696(1)	0.43129(1)	1.01(6)
Si(1)	0.47458(1)	0.22386(1)	0.11329(1)	1.41(8)
Si(2)	0.40727(1)	0.51762(1)	0.03687(2)	1.60(8)
Si(3)	0.10208(1)	0.17049(1)	0.09229(2)	1.60(7)
Si(4)	0.47110(1)	0.49332(1)	0.47400(1)	1.29(7)
Si(5)	0.36011(1)	0.23342(1)	0.52505(1)	1.32(7)
Si(6)	0.21244(1)	0.34570(1)	0.50542(2)	1.51(8)
C11	0.4689(4)	0.3251(4)	0.1779(5)	1.40(2)
C12	0.4101(5)	0.1120(5)	0.1983(6)	2.0(3)
C13	0.6034(5)	0.2539(5)	0.1005(6)	2.3(3)
C14	0.4189(5)	0.1969(5)	-0.0285(6)	2.3(3)
C21	0.3187(4)	0.4424(4)	0.1435(5)	1.5(3)
C22	0.5293(5)	0.5930(5)	0.0995(7)	2.1(3)
C23	0.4172(5)	0.4410(5)	-0.0740(5)	2.5(3)
C24	0.3711(5)	0.5996(6)	-0.0317(6)	2.9(4)
C31	0.1981(4)	0.1769(4)	0.1842(5)	1.7(3)
C32	0.1512(5)	0.2247(6)	-0.0456(6)	2.8(3)
C33	0.0048(5)	0.0423(5)	0.0687(6)	2.1(3)
C34	0.0422(5)	0.2339(5)	0.1564(7)	2.8(4)
C41	0.4416(5)	0.5876(5)	0.4350(6)	2.4(3)
C42	0.5783(4)	0.5116(5)	0.3936(5)	1.8(3)
C43	0.5004(5)	0.5065(5)	0.6243(5)	2.1(3)
C51	0.4848(5)	0.2575(5)	0.5019(6)	2.0(3)
C52	0.3392(5)	0.2346(5)	0.6760(6)	2.3(3)
C53	0.2719(5)	0.1128(5)	0.4659(6)	2.0(3)
C61	0.2352(5)	0.3948(6)	0.6498(6)	2.7(4)
C62	0.1107(5)	0.2188(5)	0.5081(7)	2.6(3)
C63	0.1782(5)	0.4177(5)	0.4149(6)	2.2(3)

$^aB_{iso}$ = the mean of the principal axes of the thermal ellipsoid

Abstract for inclusion in ChemAbstracts

Abstract—The reaction of $(Me_3SiCH_2)_3Ga$ with $P(SiMe_3)_3$ or $As(SiMe_3)_3$ in a 1:1 mole ratio affords the simple adducts $(Me_3SiCH_2)_3Ga{\bullet}P(SiMe_3)_3$ (**1**) and $(Me_3SiCH_2)_3Ga{\bullet}As(SiMe_3)_3$ (**2**), respectively. Combining $(Me_3SiCH_2)_3In$ with $P(SiMe_3)_3$ in a 1:1 mole ratio yields the adduct $(Me_3SiCH_2)_3In{\bullet}P(SiMe_3)_3$ (**3**), in a nearly quantitative yield.

The solid-state structures of **1** and **3** were established by X-ray crystallography. Isomorphous **1** and **3** crystallize in the trigonal system, space group $P3_1$, with a = 16.027(3), c = 11.9928(18) Å, V = 2667.9(7) $Å^3$, Z = 3, $D_{calc.}$ = 1.087 g cm^{-3} for **1**, and a = 16.061(8), c = 12.0913(19) Å, V = 2701.0(13) $Å^3$, Z = 3, $D_{calc.}$ = 1.156 g cm^{-3} for **3**. Full-matrix least-squares refinement based on 3397 (**1**) and 4156 (**3**) reflections with $I > 2.5\sigma$ converged at R = 0.059 (R_w = 0.062) and R = 0.039 (R_w = 0.044), respectively. Metal-pnicogen-bond lengths were found to be: Ga-P = 2.646 Å, and In-P = 2.771 Å. The thermal decomposition behavior of **1** - **3** was examined by TGA-DTA. These studies indicated that compounds **1** and **2** eliminated their organic ligands in a stepwise manner, while compound **3** decomposed in a single-step process.

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